Microplastics Analysis and the Infrared Spectrum: Is Spectral Range Selection Critical?

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Introduction

Microplastic contamination is an emerging threat to environmental and ecological systems across the globe. Microplastics are defined as small (less than 5 mm) solid fragments of synthetic or modified natural polymers that are insoluble in water.[1] Studies have shown that plastic particles cause harm to multiple types of organisms through exposure to toxic substances.[2,3] Despite these known toxic effects, the full extent of the impact of microplastics remains unclear due to challenges in developing reliable methods for characterizing this broad class of micro-sized polymers.

Infrared (IR) spectroscopy is an established technique for characterizing microplastics. It identifies the molecular composition and structure of materials by measuring the absorption of IR radiation. The resulting absorption bands, which are due to intramolecular vibrational modes, help identify organic or mineral materials through comparison of spectra with a library of spectra from known polymers.[1] Current directives and standard methodologies require that major types of polymers are identified correctly and can be distinguished from other natural materials.[1,4]

Major types of polymers include polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS), polyvinylchloride (PVC), polyamide (PA), polyurethane (PU), polymethylmethacrylate (PMMA), polytetrafluoroethylene (PTFE), and polycarbonate (PC). These polymers provide IR information in five spectral ranges[5] as follows:

- 2,980 to 2,780 cm^{-1} (stretching vibrations of CH/CH$_2$/CH$_3$ groups)
- 1,480 to 1,400 cm^{-1} (CH$_2$ bending vibrations)
- 1,760 to 1,670 cm^{-1} (C=O stretching vibrations)
- 1,800 to 1,740 cm^{-1} (C=O stretching vibrations)
- 1,260 to 1,087 cm^{-1} (CF$_2$ stretching vibrations)

Figure 1 shows spectra of the most common synthetic polymers acquired by FTIR in attenuated total reflectance (ATR) mode.

IR spectral acquisition is typically performed between 750 and 4,000 cm^{-1}; however, only specific regions are used for the identification of microplastics. These spectral ranges are selected based on considerations such as exclusion of regions with a low signal-to-noise ratio (S/N), substrate or filter limitations, or instrument manufacturer specifications.

This study investigated the impact of narrowing the IR spectral range on the identification of microplastics using three data collection modes and multiple spectral ranges. All experimental work was applied to the same materials.

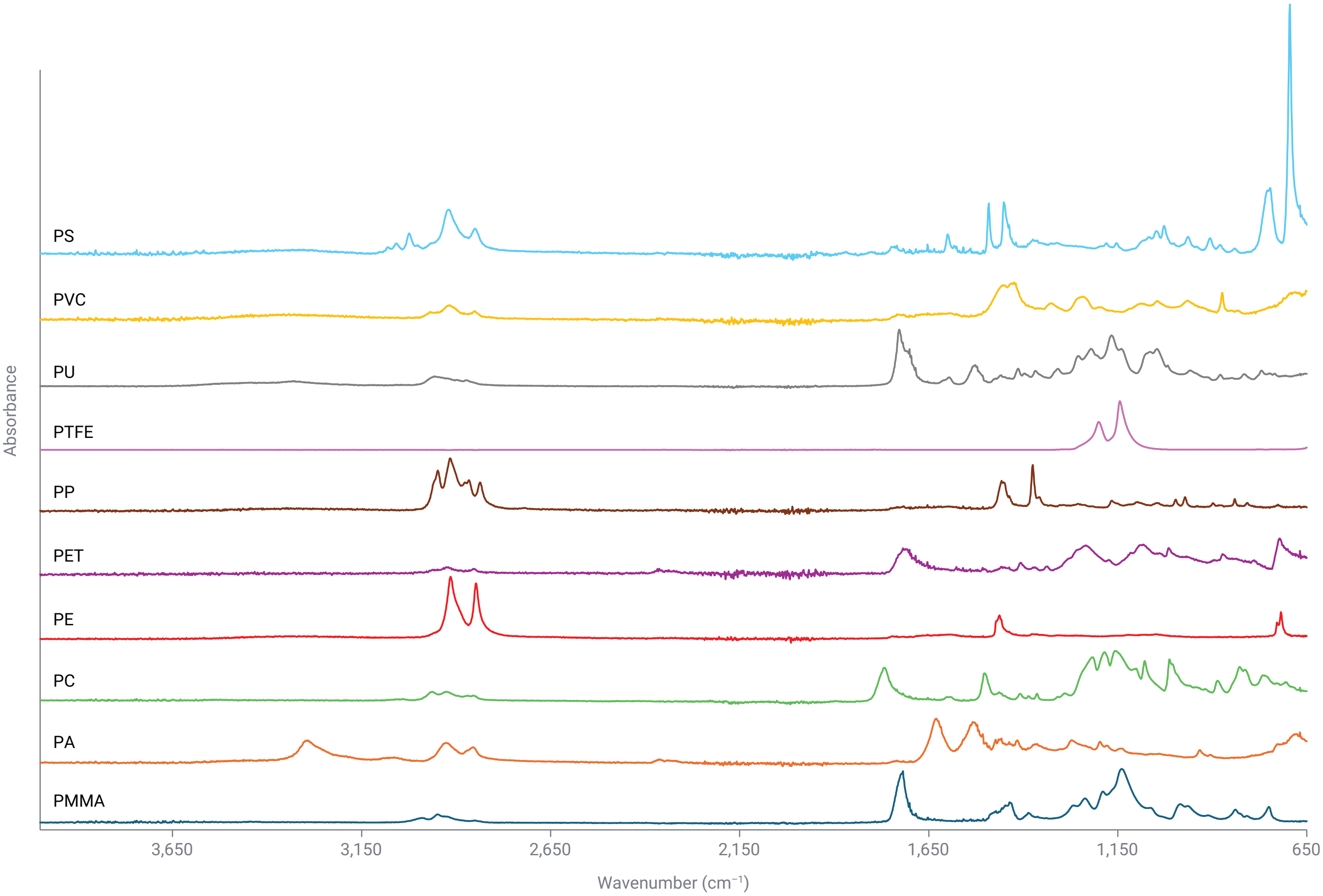


Figure 1. FTIR spectra of the most common synthetic polymers measured using the Agilent Cary 630 FTIR-ATR.

Experimental

Sample and sample preparation

Plastic pellets (sourced from SP2 Scientific Polymer Products Inc, New York State, USA; Polymer Sample Kit, part number 205) and items of known polymer type were ground into a powder using a metallic file. Single particles of these samples were analyzed by FTIR-ATR (Cary 630 FTIR).

For microplastics imaging analysis, the particles of each polymer type were collected in a vial containing absolute ethanol (CAS No. 64-17-5). After vigorous shaking, 20 µL of the suspension was transferred onto low-e reflective IR slides using a pipette, ready for analysis.

Instrumentation

To evaluate the effects of narrowing the IR spectral range on microplastics identification, a comparative study was performed using the following three systems:

- Agilent Cary 630 FTIR with an ATR module, covering 650 to 3,945 cm^{-1}.
- Agilent Cary 620 FTIR microscope coupled with an Agilent Cary 670 FTIR spectrometer (product discontinued), covering 650 to 3,945 cm^{-1}.
- Agilent 8700 LDIR chemical imaging system, operating within 975 to 1,800 cm^{-1}.

For data collection by the Cary 630 FTIR-ATR, a particle from each material with a diameter > 500 µm was placed on the platform and measured directly using the operating parameters given in Table 1.

Table 1. Agilent Cary 630 FTIR-ATR operating parameters.

Parameter	Setting
Background Scans	64
Sample Scans	64
Spectral Resolution	2 cm^{-1}
Spectral Range	650 to 4,000 cm^{-1}
Mode of Measurement	ATR
Background	Air

For the two imaging systems, a selected area of the low-e IR slide of each polymer was analyzed using the operating conditions given in Tables 2 and 3.

Table 2. Parameters used for the Agilent Cary 620 FTIR microscope coupled to an Agilent Cary 670 FTIR.

Parameter	Setting
Focal Plane Array (FPA) Size	128 × 128
Objective	15x
IR Pixel Size	5.5 µm
Number of Scans Per Tile	120
Spectral Resolution	2 cm^{-1}
Spectral Range	650 to 3,954 cm^{-1}
Mode of Measurement	Reflection
Substrate/Background	Low-e slide

Table 3. Parameters used for the Agilent 8700 LDIR automated method analysis of microplastics.

Parameter	Setting
Method	Particle Analysis
Minimum Particle Size	20 µm
Maximum Particle Size	500 µm
Scan Speed	Default (8)
Sweep Speed	Default (3, high speed)
Focus Offset	0
Polarization (Degree)	Default (0)
Attenuation (%)	Default (0)/Auto
Spectral Resolution	0.5 cm^{-1}
Spectral range	975 to 1,800 cm^{-1}
Mode of Measurement	Reflection
Substrate/Background	Low-e slide
Number of Scans Per Particle	1

Data processing

Polymer identification and correlation calculations for each technology were performed by exporting spectra, converting reflection data to absorbance, and calculating the first derivative (Microsoft Excel for Microsoft 365 MSO Version 2409 Build 16.0.18025.20214). The resulting data were then correlated with reference library spectra using Pearson's method.[6] The siMPle library, containing 326 ATR spectra of commonly encountered environmental polymers, was used for this analysis.[7] For data obtained from the Cary 620 FTIR microscope imaging system, the CO_2 absorption region (2,250 to 2,450 cm^{-1}) was flattened before applying the correlation.

Results and discussion

Spectral range selection

To investigate the effects of reducing the spectral range on the identification and correlation values, four regions were selected for the Cary 630 and Cary 620 datasets as follows:

- **Full spectral range:** 650 to 3,945 cm^{-1}
- **Avoidance of low S/N range:** 950 to 3,590 cm^{-1}
- **Anodisc filters range:** 1,250 to 3,590 cm^{-1}
- **Fingerprint region:** 975 to 1,800 cm^{-1}

Cary 630 FTIR-ATR

All polymers were identified correctly using the Cary 630 FTIR-ATR regardless of the spectral range used, as shown in Table 4. There was only a minor change in the specific identification across the ranges, but not necessarily the major polymer group. The main findings regarding spectral correlations over different spectral ranges include:

- Minimal variation was observed in correlation values for PMMA, PC, PE, and PU across all four evaluated spectral ranges.
- Narrowing the spectral range to 975 to 1,800 cm^{-1} (the fingerprint region) resulted in improved correlation for PA, PP, and PVC, while maintaining consistent values for the other polymers.
- PET and PS achieved the highest correlation values in both the full spectral range (650 to 3,945 cm^{-1}) and the narrowest range (975 to 1,800 cm^{-1}) compared to the intermediate ranges (950 to 3,590 cm^{-1} and 1,250 to 3,590 cm^{-1}).
- PTFE demonstrated optimal performance at 975 to 1,800 cm^{-1}, achieving a correlation of 0.9782, indicating excellent compatibility with the reduced range. This result is mainly driven by the CF$_2$ stretching vibration below 1,250 cm^{-1}.

Correlation values are generally comparable or improved for polymers such as PMMA, PTFE, and PVC in the fingerprint range, suggesting that this narrower range of 975 to 1,800 cm^{-1} provides sufficient information for polymer identification in many cases.

Table 4. Impact of spectral range on identification and correlation using an Agilent Cary 630 FTIR-ATR.

Polymer	650 to 3,945 cm^{-1}	950 to 3,590 cm^{-1}	1,250 to 3,590 cm^{-1}	975 to 1,800 cm^{-1}
PS	0.95 Polystyrene	0.78 Polystyrene	0.78 Polystyrene	0.84 Polystyrene
PE	0.81 Polyethylene_low_density	0.81 Polyethylene_low_density	0.81 Polyethylene_low_density	0.82 Polyethylene_low_density
PET	0.61 Poly(ethylene_terephthalate)	0.54 Poly(ethylene_terephthalate)	0.47 Fibre_polyester	0.62 Poly(ethylene_terephthalate)
PC	0.89 Polycarbonate	0.90 Polycarbonate	0.87 Polycarbonate	0.91 Polycarbonate
PVC	0.28 Poly(vinyl_chloride)_carboxylated	0.30 Polyvinylchloride_with_plasticizer	0.26 Polyvinylchloride_with_plasticizer	0.60 Polyvinylchloride_with_plasticizer
PP	0.79 Fibre_polypropylene_dyed	0.80 Fibre_polypropylene_dyed	0.80 Fibre_polypropylene_dyed	0.94 Fibre_polypropylene_dyed
PTFE	0.96 Poly(tetrafluoroethylene)	0.97 Poly(tetrafluoroethylene)	0.36 Poly(tetrafluoroethylene)	0.98 Poly(tetrafluoroethylene)
PA	0.51 Nylon_6_6	0.51 Nylon_6_6	0.50 Nylon_6_6	0.72 Nylon_6_6
PU	0.77 Polyurethane	0.78 Polyurethane	0.76 Polyurethane	0.82 Polyurethane
PMMA	0.85 Polymethyl methacrylate	0.86 Polymethyl methacrylate	0.83 Polymethyl methacrylate	0.88 Polymethyl methacrylate

Correlation	< 0.4	0.4 to 0.6	0.6 to 0.8	> 0.8

Cary 620 FTIR microscope imaging

As with the Cary 630 data, all polymers were correctly identified using the Cary 620 FTIR microscope imaging system. However, the full spectral range (650 to 3,945 cm^{-1}) exhibited the lowest correlation values, primarily due to low S/Ns at the spectrum's extremities. Narrowing the range to 950 to 3,590 cm^{-1} improved the correlation, as shown in Table 5.

Key observations from the reduced spectral range study include:

- Minimal variation was observed in correlation values for PA, PC, PE, PET, PMMA, PS, PU, and PVC across the three evaluated spectral ranges.
- Narrowing the spectral range to 975 to 1,800 cm^{-1} resulted in improved correlation for PP and PTFE while maintaining consistent identification results.

Table 5. Impact of spectral range on identification and correlation using an Agilent Cary 620 FTIR microscope imaging system.

Polymer	650 to 3,945 cm^{-1}	950 to 3,590 cm^{-1}	1,250 to 3,590 cm^{-1}	975 to 1,800 cm^{-1}
PS	0.41 Polystyrene	0.80 Polystyrene_expanded	0.79 Polystyrene_expanded	0.84 Styrene_acrylonitrile
PE	0.41 Polyethylene_low_density	0.61 Polyethylene_low_density	0.63 Polyethylene_low_density	0.69 Polyethylene_foamed
PET	0.54 Polyethylene terephthalate	0.63 Polyethylene terephthalate	0.57 Polyethylene terephthalate	0.63 Polyethylene terephthalate
PC	0.37 Polycarbonate	0.55 Polycarbonate	0.60 Polycarbonate	0.58 Polycarbonate
PVC	0.17 Vinyl_chloride_vinyl_acetate_ hydroxypropyl_acrylate	0.38 Vinyl_chloride_vinyl_acetate_ hydroxypropyl_acrylate	0.38 Polyvinylchloride	0.47 Vinyl_chloride_vinyl_acetate_ hydroxypropyl_acrylate
PP	0.62 Polypropylene	0.71 Polypropylene	0.70 Fibre_polypropylene	0.88 Polypropylene
PTFE	0.14 Polytetrafluoroethylene	0.44 Polytetrafluoroethylene	0.37 Poly(tetrafluoroethylene)	0.67 Polytetrafluoroethylene
PA	0.43 Nylon_6_6	0.71 Nylon_6_6	0.71 Nylon_6_6	0.74 Nylon_6_6
PU	0.46 Alkyd_varnish	0.61 Alkyd_varnish	0.70 Alkyd_varnish	0.61 Alkyd_varnish
PMMA	0.31 Polymethyl methacrylate	0.38 Polymethyl methacrylate	0.36 Polymethyl methacrylate	0.39 Polymethyl methacrylate

Correlation	< 0.4	0.4 to 0.6	0.6 to 0.8	> 0.8

8700 LDIR chemical imaging system

The 8700 LDIR uses a tunable quantum cascade laser (QCL) IR source to scan the fingerprint region (975 to 1,800 cm^{-1}) at any sample location, generating molecularly specific spectral signatures for polymer identification. Using Pearson's correlation, similar to the other technologies, the exported LDIR data accurately identified all polymers, as shown in Table 6. The correlation values ranged from 0.629 to 0.964.

Table 6. Identification and correlation results using an Agilent 8700 LDIR data processed using Pearson's method.

Polymer	975 to 1,800 cm^{-1}
PS	0.94 Polystyrene
PE	0.92 Polyethylene_low_density
PET	0.82 Polyethylene_terephthalate
PC	0.92 Polycarbonate
PVC	0.74 Polyvinylchloride
PP	0.96 Polypropylene
PTFE	0.63 Polytetrafluoroethylene
PA	0.90 Nylon_6_6
PU	0.75 Polyurethane
PMMA	0.73 Polymethyl methacrylate

Correlation	< 0.4	0.4 to 0.6	0.6 to 0.8	> 0.8

The same LDIR spectra were analyzed using the automated Particle Analysis workflow in the Agilent Clarity software, where matching is based on the cosine similarity of the first derivative of the spectra. The analysis uses the high-quality Microplastics Starter 2.1 library supplied with Agilent Clarity software, which contains spectral data for polymers and natural materials.[7,8]

As summarized in Table 7, this method achieved accurate identification results for all polymers, as indicated by hit quality index (HQI) scores between 0.878 and 0.987. (High confidence HQI scores range from 0.85 to 0.99 and a score of 1 represents the highest quality result).

Table 7. Polymer identification and HQI results for spectra acquired using an Agilent 8700 LDIR processed by Agilent Clarity software and the Particle Analysis workflow.

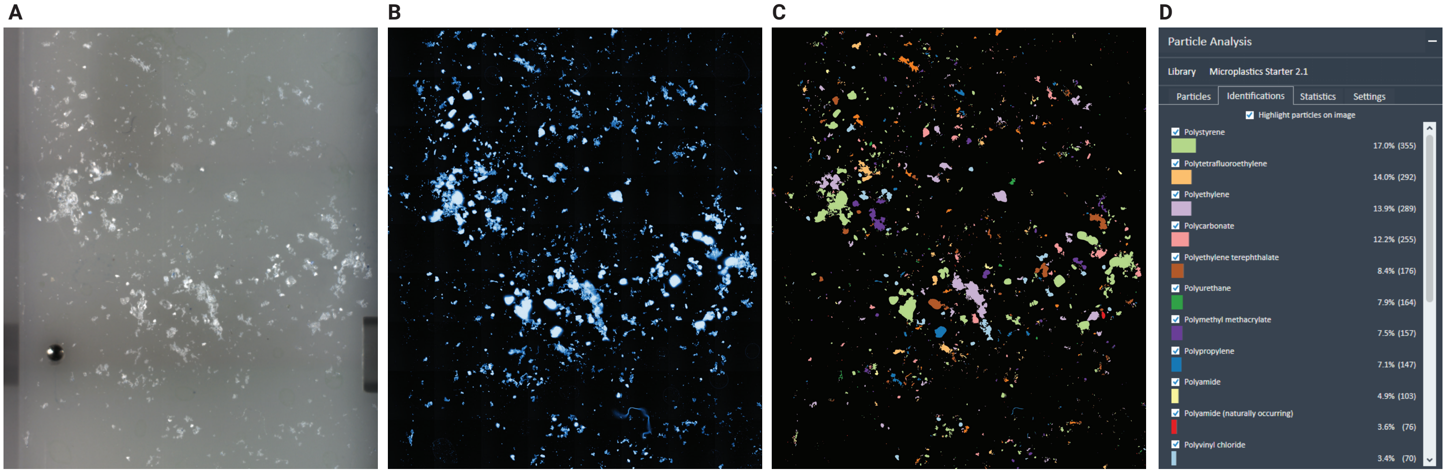
Polymer	Microplastics Starter library 2.1 and Clarity HQI
PS	0.978 Polystyrene
PE	0.987 Polyethylene
PET	0.954 Polyethylene terephthalate
PC	0.953 Polycarbonate
PVC	0.878 Polyvinylchloride
PP	0.984 Polypropylene
PTFE	0.976 Polytetrafluoroethylene
PA	0.964 Polyamide
PU	0.943 Polyurethane
PMMA	0.952 Polymethyl methacrylate

As a dedicated system for microplastics characterization, the 8700 LDIR (Figure 2) uses fully automated workflows that enable significantly faster analysis times than FTIR imaging. Also, as shown in Table 7 and Figure 3, there is no need for external data processing, as the software includes a tailored microplastics library that facilitates the accurate identification of polymers. The library match result is quality-assured using the HQI score system.

LDIR hit quality index (HQI) matching is based on the cosine similarity of the first derivative of a spectrum, with scores from 0.85 to 0.99 indicating high confidence matches, and 1.00 as the highest quality. It is designed for the automated Particle Analysis workflows and optimized for spectral comparisons in microplastics analysis, ensuring robust and accurate identification.

Pearson correlation coefficient measures the linear correlation between two variables, with values ranging from –1 (perfect negative correlation) to 1 (perfect positive correlation). It predicts how changes in one variable will affect another and is widely used in statistical and scientific analyses. However, it may not capture the specific nuances of spectral data.

Figure 2. The Agilent 8700 LDIR Chemical Imaging System allows the high-speed routine analysis of microplastics, including the number of particles present in the sample, their size, and their chemical composition.



Library Microplastics Starter 2.1

☑ Highlight particles on image

☑ Polystyrene	🟩	17.0% (355)
☑ Polytetrafluoroethylene	🟧	14.0% (292)
☑ Polyethylene	🟪	13.9% (289)
☑ Polycarbonate	🟥	12.2% (255)
☑ Polyethylene terephthalate	🟫	8.4% (176)
☑ Polyurethane	🟩	7.9% (164)
☑ Polymethyl methacrylate	🟪	7.5% (157)
☑ Polypropylene	🟦	7.1% (147)
☑ Polyamide	🟨	4.9% (103)
☑ Polyamide (naturally occurring)	🟥	3.6% (76)
☑ Polyvinyl chloride	🟦	3.4% (70)

Figure 3. Identification and classification data for a microplastics mixture analyzed on low-e reflective IR slide using an Agilent 8700 LDIR system (39 × 23 mm area). (A) Visible image of the analyzed area. (B) IR image scanned at 1,442 cm^{-1}. (C) Highlights of particles found—the particles are colored based on the identification of the type of microplastics. (D) Automatic statistical data generated based on the identification of microplastics.

Conclusion

Infrared (IR) spectroscopy was used to characterize the major types of microplastics by identifying their polymer composition through spectral analysis. The critical role of spectral range selection in achieving accurate identification of microplastics was highlighted by spectral data collected using different measurement modes and technologies. These various methods were conducted using an Agilent 630 FTIR, Agilent Cary 620 FTIR microscope coupled to an Agilent Cary 670 FTIR, and an Agilent 8700 LDIR chemical imaging system.

All the major types of polymers were successfully identified using each technique when the spectral range was narrowed to the fingerprint region (975 to 1,800 cm^{-1}). Since this is the spectral range used by the 8700, the study establishes LDIR as a reliable technique for the characterization of microplastics.

The polymer identification and HQI results show the value of the 8700 LDIR's tailored microplastics library in delivering comprehensive and accurate identification of microplastics. Also, the instrument's automated workflow ensures high efficiency in characterizing microplastics across diverse matrices, offering rapid analysis times and high sample throughput.

The unique design and performance features of the 8700 LDIR make it an excellent choice for routine applications and large-scale monitoring studies focused on the characterization of microplastics.

References

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Further information

- Agilent 8700 LDIR Chemical Imaging System
- Agilent Clarity Software
- Microplastics Technologies FAQs
- Microplastics Analysis in Water

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DE-003281

Printed in the USA, January 14, 2025
5994-8037EN

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